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Gauss' Principle and Statistical Thermodynamics

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Abstract. A foundation of statistical thermodynamics without using the microstructure of a thermodynamic system has been built up on the basis of Gauss' principle of arithmetic mean.

1. INTRODUCTION

In statistical mechanics there are a number of extreme principles characterising the statistical equilibrium of a thermodynamic system [1-4]. The maximum-entropy principle is, however, the best well known of them all. The Gauss' principle of arithmetic mean - first postulated by Gauss in the study of error of observation, is also an important estimation principle [5]. Its equivalence with the principle of maximum-entropy estimation as well as its importance in the foundation of statistical thermodynamics was first studied by Dutta [2]. In this paper we shall present a statistical theory of thermodynamics on the basis of Gauss'principle of arithmetic mean. The theory in the spirit of an essentially statistical theory is independent of the microstructure of the system. The present paper is a modification of the earlier paper [6].

2. THERMODYNAMIC MEASUREMENT: STATISTICAL MODEL

Let us consider a finite system. The system is brought in thermal equilibrium with very large system (heat-reservoir) $R(\theta)$ of temperature θ. The temperature or the parameter θ is usually unknown and the problem is to measure it. For this the finite system may be considered as a thermometer to measure the temperature or parameter θ of the heat reservoir $R(\theta)$. This consists in separating the system from the heat reservoir $R(\theta)$ after a sufficiently large time and ascertaining its energy [6,7]. The determination of the parameter θ is thus equivalent to the problem of estimation of θ from the observed values of the energy. This is a problem of parameter estimation in mathematical statistics and as pointed out by Mandelbrot [8] it is the proper statistical counterpart of thermometry.

Let X represent the energy of the system and be the only macroscopically measurable characteristic of the system. Due to the random interaction of the system with the heat-reservoir $R(\theta)$, the energy X is assumed to be governed by a random process. This is our basic assumption about the stochastic nature of thermal equilibrium.Let $P(X|\theta)$ be the probability distribution of the energy X of the system conditioned by the parameter θ of the heat-reservoir $R(\theta)$. Let us assume the reproducibility of the experiment or measurement that is, we assume that the experiment can be repeated on a large number of times. Let $\underline{X} = (X_1, X_2, \ldots, X_N)$ be the observed values of X. The probability distribution of the observed values $\underline{X} = (X_1, X_2, \ldots, X_N)$ is given by

$$\rho(\underline{X}|\theta) = \prod_{i=1}^{N} P(X_i|\theta) \tag{1}$$

When the form of the probability distribution $P(X_i|\theta)$ is known, the estimation of the parameter is as usual. But we have the converse problem that is, we have to estimate the probability distribution $P(X_i|\theta)$ subject to some information or data about the parameter or temperature θ.

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3. Gauss'Principle and Law of Probability Distribution

The fundamental problem of statistical thermodynamics is to find the law of probability distribution $P(X|\theta)$ subject to some prior information or data. We ask for the temperature that yields an average $\langle X\rangle = E(\theta)$ identical to the empirical one i.e. the arithmetic mean $\overline{X} = \frac{1}{N}\sum_{i=1}^{N} X_i$ so that we have [7]

$$\frac{1}{N}\sum_{i=1}^{N} X_i = E(\theta) \quad \text{or} \quad \sum_{i=1}^{N}(X_i - \langle X\rangle) = 0 \tag{2}$$

which constitutes the information or constraint about the system. To find the law of probability distribution we shall use Gauss'principle of arithmetic mean which states that "for a set of observations of an unknown magnitude of a physical quantity, the probability distribution would be maximum when the best estimate of the location parameter would be the arithmetic mean "[5]. We now assume that the average $\langle X\rangle$ acts as the location parameter of the distribution P$(X|\theta)$. The estimation of P$(X|\theta)$ according to Gauss' principle, then consists in selecting that probability distribution which would maximize P or $\log P$ subject to the constraint (2). Using Lagrange's undetermined multiplier $\lambda(\theta)$ and taking variation with respect to the location parameter $\langle X\rangle$, we have

$$\begin{aligned} \frac{\partial}{\partial\langle X\rangle}\left[\log P - \lambda(\theta)\sum_{i=1}^{N}(X_i - \langle X\rangle)\right] &= 0 \\ \text{or} \quad \frac{\partial}{\partial\theta}\left[\log P - \lambda(\theta)\sum_{i=1}^{N}(X - \langle X\rangle)\right] &= 0 \end{aligned} \tag{3a}$$

so that we have

$$\frac{\partial}{\partial\theta}\log \mathrm{P}(X_i|\theta) = \frac{d\lambda(\theta)}{d\theta}(X_i - \langle X\rangle) - \lambda(\theta)\frac{d\langle X\rangle}{d\theta} \tag{3b}$$

which leads to the probability distribution

$$P(X_i|\theta) = e^{\lambda(\theta)X_i}h(X_i)|Z(\lambda(\theta)) \tag{4}$$

where $Z(\lambda(\theta)) = \int e^{\lambda(\theta)X}h(X)dX$ is the normalising factor. With the help of the second law of thermodynamics it can be shown that $\lambda(\theta)$ is a universial function having the form [9]

$$\lambda(\theta) = \frac{-1}{kT} \tag{5}$$

where k is the Boltzmann constant and T is the absolute temperature. The distribution (4) is the Gibbs' canonical distribution of energy.

4. Thermodynamic Limit: Maximum-likelihood Principle

Let us now consider the thermodynamic limit or asymptotic case of a large system, in that the case deviation in the observed values X_i of the extensive variable X from $\langle X\rangle$ is negligibly small and the system practically reduces to an isolated system. For such an asymptotic case, the terms $X_i - \langle X\rangle$ in the r.h.s. of (4) become zero and the equation (4) reduces to

$$\frac{\partial}{\partial\theta}\log \mathrm{P}(\underset{\sim}{X}|\theta) = 0 \tag{6}$$

which is the maximum-likelihood equation for the estimation of the parameter θ or $\lambda(\theta)$. Let $\hat{\lambda}(\theta)$ be the maximum-likelihood estimate of $\lambda(\theta)$ i.e. the value of $\lambda(\theta)$ determined by (6). Let us use this property to find the probability of fluctuation. Let $\Delta\hat{\lambda}$ be the deviation in the value of $\hat{\lambda}$ due to spontaneous fluctuation in thermal equilibrium. Then a measure of distance Δs between the states corresponding to the parametric values $\hat{\lambda}$ and $\hat{\lambda} + d\hat{\lambda}$ is, for N independent observation, given by [10]

$$\Delta s^2 = NH_X(\hat{\lambda})(\Delta\hat{\lambda})^2 \tag{7}$$

where

$$H_X(\hat{\lambda}) = \int \left[\frac{\partial}{\partial\hat{\lambda}} \log \mathrm{P}(X|\hat{\lambda})\right]^2 \mathrm{P}(X|\hat{\lambda})dX \tag{8}$$

is the Fisher information. For small $\Delta\hat{\lambda}$, the distance Δs given by (7) defines the well-known Riemannian geometry [10]. For large N, the maximum-likelihood estimate $\hat{\lambda}$ is distributed normally and the distance Δs^2 given by (7) has an asymptotic normal $N(0,1)$ distribution [12] so the probability of fluctuation is given by

$$P(\Delta\hat{\lambda}) \sim \exp\left\{-\frac{1}{2}H_X(\hat{\lambda})(\Delta\hat{\lambda})^2\right\} = \exp\left\{-\frac{1}{2}\left(\frac{d\langle X\rangle}{d\hat{\lambda}}\right)^2(\Delta\hat{\lambda})\right\} \tag{9}$$

where we have used the canonical distribution of energy X of the system. So the fluctuation of $\hat{\lambda}$ is given by

$$\operatorname{var}(\hat{\lambda}) = \langle(\Delta\hat{\lambda})^2\rangle = \frac{\left(\frac{d\langle X\rangle}{d\hat{\lambda}}\right)^2}{\operatorname{var}(X)} = \frac{1}{kT^2 c_v} \qquad \text{or} \qquad \operatorname{var}(T) = \frac{kT^2}{c_v} \tag{10}$$

where c_v is the specific-heat at constant volume. Thus the Gaussian distribution (9) and the fluctuation formula (10) determine the statistical character of the temperature of a thermodynamically large or an isolated system. Thus, while the Gauss' principle of arithmetic mean characterizes the statistical equilibrium of a closed system, it is the maximum-likelihood principle that characterizes the statistical equilibrium of an isolatedsystem in the thermodynamic limit of a large system [6].

5. Conclusion

The theory based on Gauss' principle of arithmetic mean is independent of any mechanical model of the system. This is in the spirit of the fundamental work of Szilard [8] who first pointed out the possibility of building up the foundation of statistical thermodynamics without using the microstructure of the system. In the thermodynamic limit of a large system the Gauss' principle leads to the principle of maximum-likelihood principle characterising the statistical equilibrium of an isolated system [6,7].

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